OPTIMIZATION OF TITANIUM DIOXIDE (TiO_2) THIN FILM USING DIP COATING TECHNIQUE FOR OXYGEN GAS SENSOR

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In the name of Allah, Most Gracious, The Most Merciful

All Praise to Allah

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ABSTRACT

Titanium dioxide (TiO_2) thin film gas sensors have been widely used and investigated in the detection of target gases. However, to obtain anatase phase for oxygen gas sensor with low and short annealing temperature is the obstacle in the fabrication of oxygen gas sensor. It is thus desirable to develop TiO_2 thin film preparation technique that provides the anatase phase for oxygen gas sensor at low and short annealing temperature. In this study, the dip coating method was used to fabricate the TiO_2 thin film. The parameters such as deposition layer, withdrawal speed of dip coating and annealing temperature were varied to optimize the properties of thin film. The optimum parameters are obtained from the 1 layer deposition film, 10 mm/ min withdrawal speed of dip coating, and annealed the film at 400 °C in electrical furnace. Crystal structure studies showed that the optimized TiO_2 thin film is anatase phase with tetragonal lattice structure and (101) plane is the dominant peak. Morphological studies indicated that the film is even and uniform in manner with grain size of 13.3 nm. The crystallite size obtained from HIGHSCORE software is 69.02 nm and calculated crystallite size using Scherrer's equation is 55.7 nm. The electrical studies showed that the film resistivity is 1.64 x 10^{-3} Ω.cm. The gas sensor measurement revealed that the response and recovery time of TiO_2 thin film sensor at room temperature is about 13.22 s and 2.67 s, respectively. Thus, proving that the potential to use the TiO_2 thin film fabricated by dip coating as active layer in oxygen gas sensor.

ABSTRAK

Pengesan gas daripada filem nipis titanium dioksida (TiO_2) telah digunakan dengan meluas dan dikaji kebolehannya. Walau bagaimanapun, untuk memperoleh fasa anatas untuk digunakan pada pengesan gas dengan suhu penyepuhlindapan yang rendah dan masa penyepulindapan yang singkat merupakan suatu halangan dalam pemfabrikatan pengesan gas oksigen. Oleh itu, menjadi suatu keperluan untuk membaiki teknik penyediaan bagi menghasilkan filem nipis TiO_2 fasa anatas untuk pengesan gas oksigen. Dalam kajian ini, teknik penyalutan celup telah digunakan. Bagi mendapatkan filem yang optimum, parameter seperti lapisan pengendapan, kelajuan penarikan penyalutan celup dan suhu penyepuhlindapan telah diubah. Parameter yang optimum telah diperoleh iaitu satu lapisan pengendapan, 10 mm/min kelajuan penarikan dan 400 ˚C suhu penyepuhlindapan dalam relau elektrik. Kajian struktur kristal menunjukkan filem nipis TiO_2 yang optimum merupakan fasa anatas yang mempunyai struktur kekisi tetragon dengan satah (101) adalah puncak dominan. Kajian morfologi menunjukkan filem sekata dengan saiz butir 13.3 nm. Saiz kristalit daripada perisian HIGHSCORE ialah 69.02 nm dan saiz kristalit dari hasil pengiraan persamaan Scherrer ialah 55.7 nm. Kajian elektrikal menunjukkan kerintangan filem ialah 1.64 x 10^{-3} Ω.cm. Pengukuran pengesan gas menunjukkan masa gerak balas dan pemulihan pada suhu bilik masing-masing ialah 13.22 s dan 2.67 s. Oleh itu, kajian ini membuktikan keupayaan filem nipis TiO_2 hasil pemfabrikatan teknik penyalutan celup sebagai lapisan aktif dalam pengesan gas oksigen.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

AFM	-	Atomic force microscope
Al	-	Aluminium
Al_2O_3	-	Aluminium oxide
Ar	-	Argon
Au	-	Gold
CH_3	-	Methane
CO	-	Carbon monoxide
CTE	-	Coefficient thermal expansion
CVD	-	Chemical vapour deposition
D	-	Crystallite size
DC	-	Direct current
EDAX	-	Energy dispersive analysis of x-rays
E_g	-	Band gap energy
eV_s	-	Potential barrier
FESEM	-	Field emission scaning electron microscope
FWHM	-	Full width at half maximum
Ge	-	Germanium
H_2	-	Hydrogen
H_2S	-	Hydrogen sulfide
HCl	-	Hydrochloric acid
HF	-	Hydrofluoric acid
ICSD	-	Inorganic crystal structure database
In_2O_3	-	Indium (III) oxide
IR	-	Infrared
ITO	-	Indium tin oxide
K	-	Kelvin

KOH	-	Potassium hydroxide
$LiNbO_3$	-	Lithium niobate
M	-	Mega
N	-	Newton
N_2	-	Nitrogen
NH_3	-	Ammonia
nm	-	nanometer
NO_2	-	Nitrogen dioxide
O_2	-	Oxygen
O_3	-	Ozone
Pa	-	Pascal
Pd	-	Palladium
PEG	-	Poly ethylene glycol
ppm	-	Parts per million
PTFE	-	Poly-tetra-fluoro-ethylene
PVD	-	Physical vapour deposition
R_0	-	Resistance value immediately prior to exposure to target gas
R_a	-	Average roughness
RF	-	Radio frequency
R_g	-	Resistance value when exposed to target gas
R_q	-	Root mean square roughness
Sccm	-	Standard cubic centimeters per minute
Si	-	Silicon
SnO_2	-	Tin dioxide
SO_2	-	Sulfur dioxide
T	-	Temperature
$TiCl_3$	-	Titanium (III) chloride
TiO_2	-	Titanium dioxide
TTIP	-	Titanium tetra iso-propoxide
UHV	-	Ultrahigh vacuum
V_2O_5	-	Vanadium (V) oxide
WDAX	-	Wavelength dispersive analysis of X-rays

WO_3	-	Tungsten trioxide
XRD	-	X-ray diffraction
ZnO	-	Zinc oxide
α	-	Coefficient of linear expansion
β	-	Coefficient of volume expansion
Ω	-	Ohm
I	-	Current
V	-	Voltage
$\boldsymbol{\rho}$	-	Resistivity
$\boldsymbol{\sigma}$	-	Conductivity
π	-	22/7

LIST OF APPENDICES

LIST OF PUBLICATIONS

(i) **A.S. Bakri**, M. Z. Sahdan, F. Adriyanto, N. D. M. Said and N.A. Raship, “Influences of deposition layer on the properties of titanium dioxide thin films fabricated by dip coating technique”, ARPN Journal of Engineering and Applied Sciences, Vol. 11, No. 14, page 8834-8839, July 2016. (Q3, Scopus indexed).

(ii) **A. S. Bakri**, M. Z. Sahdan, F. Adriyanto, N. A. Raship, N. D. M. Said, S. A. Abdullah, and M. S. Rahim, “Effect of Annealing Temperature of Titanium Dioxide Thin Films on Structural and Electrical Properties”, AIP Conference Proceedings , Vol. 1788, Issue 1, No. 030030, page 1-8, January 2017.doi:10.1063/1.4968283.

(iii) N. D. Mohd Said, M. Z. Sahdan, I. Senain, **A. S. Bakri**, S. A. Abdullah, F. Mokhter, A. Ahmad and H. Saim, “Effects of Annealing Temperature on Structural, Morphology and Optical Properties of TiO_2 thin film”, ARPN Journal of Engineering and Applied Sciences, Vol. 11, No. 8, page 4924-4928, July 2016. (Q3, Scopus indexed).

(iv) N. A. Raship, M. Z. Sahdan, F. Adriyanto, M. F. Nurfazliana and **A.S. Bakri**, “The Effects of PH value on the preparation of copper oxide thin films by dip coating technique”, ARPN Journal of Engineering and Applied Sciences, Vol. 11, No. 14, page 8829-8833, July 2016. (Q3, Scopus indexed).

(v) M. S. Rahim, M. Z. Sahdan, **A. S. Bakri**, N. D. M. Said, S. H. A. Yunus, and J. Lias, “Effect of gas on the structural and electrical properties of titanium dioxide film”, AIP Conference Proceedings, Vol 1788, No. 030134, page 1-5, January 2017. doi: 10.1063/1.4968387

(vi) N. A. Raship, M. Z. Sahdan, F. Adriyanto, M. F. Nurfazliana, and **A. S. Bakri**, “Effect of annealing temperature on the properties of copper oxide films prepared by dip coating technique”, AIP Conference Proceedings, Vol 1788, No. 030121, page 1-7, January 2017. doi: 10.1063/1.4968374

(vii) N. D. M. Said, M. Z. Sahdan, A. Ahmad, I. Senain, **A. S. Bakri**, S. A. Abdullah, and M. S. Rahim”, AIP Conference Proceedings, Vol. 1788, No 030130, page 1-6, January 2017). doi: 10.1063/1.4968383

(viii) S. A. Abdullah, M. Z. Sahdan, N. Nafarizal, F. Adriyanto, H. Saim, S. N. M. Tawil, and **A. S. Bakri**, “Optimization of oxygen on Nb-doped TiO_2 using DC and RF magnetron sputtering using composite and metal target”, American Institute of Physics (AIP), Vol. 1788, No. 030112, page 1-5, January 2017. doi: 10.1063/1.4968365

(ix) **A S Bakri**, M Z Sahdan, N Nafarizal, S A Abdullah, N D M Said, N A Raship, Y Sari, “Mechanism of room temperature oxygen sensor based on nanocrystalline TiO_2 film”, Journal of Physics: Conference Series (JPCS). (Q4, Scopus indexed)

(x) S A Abdullah, M Z Sahdan, N Nafarizal, H Saim, **A S Bakri**, Cik Rohaida C H, F Adriyanto, Y Sari, “Photoluminescence study of trap-state defect on TiO_2 thin films at different substrate temperature via RF magnetron sputtering”, Journal of Physics: Conference Series (JPCS). (Q4, Scopus indexed).

(xi) Rahim, M.S., Sahdan, M.Z., **Bakri, A.S.**, Yunus, S.H.A., Lias, J,” Low Temperature Growth of High Quality Crystal of Anatase Based-TiO2 Thin Film Grown Using Double Zone CVD Technique”, Proceedings - 2016 World Symposium on Computer Applications and Research, WSCAR 2016, Vol 7791993, page 126-129, December 2016. doi: 10.1109/WSCAR.2016.23

Table A.1 : Summary of methods of fabrication titanium dioxide

Method	**Precursors**	**Synthesis conditions**	**Properties and applications**	**References**
Sol-gel dip-coating	Titanium tetra iso-propoxide (TTIP), acetyl acetone, poly ethylene glycol 400 (PEG 400) and ethanol.	Solution aging : 2 h Pre drying : 100 °C for 30 minutes. Annealing : 300- 500 ° C for 1 hour.	X- ray diffraction pattern 300 °C : the film is amorphous 400 and 500 °C : anatase phase (101) Average crystallite size : 18- 26 nm. Band gap energy : 300 °C (3.57 eV) 400 °C (3.45 eV) 500 °C (3.25 eV	[48]
	Titanium (IV) n- butoxide, 1-butanol, hydrochloric acid.	Solution aging : 2 h Temperature room : 21 °C Relative humidity : 25 % Single stage dip coating on quartz glass and silicon substrates. Withdrawal speed : 4.7 mm/s.	XRD pattern Silicon substrate : anatase phase (ICDD file No. 00-021-1272) 550 nm reference wavelength : refractive index 2.34 Crystallite size : 30 nm	[56]
	Titanium isopropoxide, acetic acid and ethanol	Solution aging : 50 minutes (fume cupboard) Substrate : ITO conducting glass Dipping speed : 2.2 mm/s	XRD : anatase phase FWHM : 0.0052 nm and 0.0069 rad I(V) characteristics : ohmic at low voltage and space charge limited (SCL) at higher voltage Thickness : 58 nm per dip	[30]

		Pulling speed : 8.4 mm/s Pre dried : ambient conditions for overnight Anneal : 550 °C for 30 minutes		
Solvothermal and hydrothermal technique	Titanium tetrasiopropoxide, 2-propanol, hydrochloric acid	Solution aging : 2 h Drying : 100 °C	X-ray diffraction file PDF # 21-1272 with 100% anatase. Peak present (101), (004), (200), (211) and (204). Crystal size ; 6.85 nm and 10.01 nm Surface area ; 159.5- 226.3 m^2/g	[49]
	Titanium isopropoxide, acetic acid, Triton x-100, 2-propanol.	Solution aging : 24 hours Hydrothermal treatment at 200 °C (~ 15 bar) for 15 hours inside an electric furnace	XRD pattern dried at 100°C : anatase phase TEM image fo 450 °C : average particle size 15-20 nm. Specific BET surface area (450 °C) : 80 m^2/g Optical band gap value : 3.36 eV	[50]
	Titanium tetrachloride, Solvents (distilled water, double distilled water, ethanol, t-butanol, sodium hydroxide and potassium hydroxide.	Solution aging : 24 hours at 150 °C Anneal : 2 hours (350 – 600 °C) Stirrer : 1- 3 hours	The smallest crystal size + highest degradation percentage : double distilled water and potassium hydroxide were used Crystallite size : anatase (14.92 nm to 27.52 nm) Rutile : 26.99 to 44.96 nm.	[42]
Sputtering	Reactive magnetron sputtering	DC input power ; 250W Oxygen partial pressure ; 1.5~23.3% Substrate ; slide glass Target-substrate spacing ; 8 cm	Mixed structure anatase and rutile Crystallite size (101) peak ; 100 nm Average grain size ; 40 nm Photocatalytic activity ; 400 nm wavelength Oxygen –defected TiO_2 photo-catalyst ; partial pressure of Ar : O_2 = 76.7:23.3 to 98.5 : 1.5 ratios.	[53]

	DC magnetron sputtering	Substrate ; aluminium AA1050 alloy and stainless steel S316L Sputtering ; industrial CemeCon CC800/9 SinOx coating unit DC input power ; 2 kW Total pressure ; 400 mPa Deposition temperature ; 150 °C Deposition rate ; 2.4 nm/ min	Anatase phase Crystallite size (101) peak : 1. 26.5 nm stainless steel 2. 25.9 nm aluminium Average base area : 1. 10,155 nm^2 on stainless steel 2. 10,010 nm^2 on aluminium Average roughness : 1. R_a = 20 nm aluminum R_z = 211.5 nm 2. R_a = 21 nm stainless steel Rz = 218.9 nm Thickness ~ 1µm	[54]
	Innovative magnetron sputtering (conventional and with modulated plasma)	Pressure in vacuum chamber ; 2 Pa Deposition time ; 120 min Working and reactive gas ; oxygen Substrate ; SiO_2 and Si	Conventional ; anatase (101) and (200) peaks ; crystallite size 26 nm With Modulated plasma ; rutile (110) and (101) peaks ; crystallite size 3 nm Thin film thickness 1. Conventional ; 650 nm 2. With modulated plasma ; 290 nm Hardness 1. Conventional ; 4.8 Gpa 2. With modulated plsma ; 16.1 Gpa	[55]

CHAPTER 1

INTRODUCTION

1.1 Introduction

A chemical gas sensor is a device that can convert concentration of target gas into an electrical signal. There are several types of chemical gas sensors such as pellistor electrochemical sensor and metal oxide semiconductor gas sensor. Metal oxide semiconductor gas sensor is also known as chemiresistor. Titanium dioxide (TiO_2) thin film is well known towards sensing different gas such as carbon monoxide (CO), oxygen (O_2), hydrogen (H_2) and carbon dioxide (CO_2). TiO_2 has recently received a great scientific interest because of its wide range of applications. TiO_2 is an n-type semiconductor and is receiving increased attention in view of its advantageous properties such as high dielectric constant [1], excellent optical transmittance [2], high refractive index [3], high chemical stability [4], and suitable energy bandgap. Interest in TiO_2 can be dated back to the early 1972 when Fujishima and Honda discovered the phenomenon of photocatalytic splitting in water into hydrogen and oxygen on a TiO_2 electrode under ultraviolet light [5]. Since then, the research of TiO_2 material is one of the widely investigated transition metal oxide by many researchers, which has led to many promising applications such as dielectric capacitor [4], optical coating layer [6], catalyst support [7], photocatalyst [8, 9] and also for gas sensor application [10].

Gas sensor has great influences in many important areas namely environmental monitoring [11, 12], domestic safety [12], public safety [13], automotive applications [11], air-conditioning in aeroplanes , and spacecrafts [14]. TiO_2 material has gained great importance in the field of gas sensor and many scientific groups are presently working on this material especially on its different nanostructures. Gas sensor devices based on TiO_2 have been successfully fabricated by other researchers. Galstyan *et al.* reported that the TiO_2 thin film is highly potential for gas sensor application. They reviewed that the surface interaction of the gas sensor is essentially the result of electronic transfer during the adsorption of gas molecules over the film surface. Its properties are based on surface interaction with reducing or oxidizing gases which as a result affects the conductivity of the film [15]. Generally, the main parameters for good sensing device performance are dependent on the size, morphology [13], intergranular connectivity, porosity, surface energy, and surface area to volume ratio of the incorporated sensing material [16].

1.2 Background study

In the early stages of research on TiO_2, this material was mostly studied in bulk form or in suspension [16]. Yadav *et al.* studied the Liquefied Petroleum Gas (LPG) sensing performances of bulk titanium dioxide and the synthesized nanostructured TiO_2 through hydrolysis of titanium trichloride ($TiCl_3$) [17]. The nanostructured TiO_2 was heat treated in a cylindrical furnace at 450 °C is having diameter of spherical grains lying between 37- 150 nm. From the XRD patterns, the diffraction pattern of bulk TiO_2 is anatase while the synthesized TiO_2 nano powder has mixed phase of anatase and rutile. The sensitivity measurement founds that the avearge sensitivities of bulk TiO_2 is 1.68 and synthesized TiO_2 is 3.0. It was found that synthesized TiO_2 has good sensor response, higher sensitivity and stability as compared to bulk titanium oxide. Sun *et al.* stated that the gas sensor in a form of bulk materials or dense film facing problem to achieve high sensitivity of gas sensor since the performance of the gas sensor is significantly influenced by the morphology and structure of the active layer [13].

Han *et al.* have synthesized and reported the nano-scale TiO_2 powders doped with phosphorus by sol-gel method for oxygen sensor [18]. The titanium trichloride and phosphoric acid were mixed with hydrochloric acid (HCl). The solution was stirred for 48 hours until it formed a gel and then dried by vacuum-drying at 80 °C. The dried powder was ground for 2 hours and finally annealed at 400 °C for 3 hours. The XRD patterns show that the pure TiO_2 is a mixture of rutile and anatase and the 5 mol % phosphorus doped TiO_2 is anatase. At low operating temperature (116 ˚C)

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